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Synthesis and Reactivity of Tungsten Vinylallene Complexes

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Protonation at one of the phenylacetylide substituents of the allylic complexes $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(C{\equiv}CPh)_2]CH_2R\}]$ (cp = $\eta\text{-}C_5H_5$), including the first cationic tungsten–ruthenium allylic vinylidene complex, R = $C(Ph){=}C{=}Ru(cp)(PPh_3)_2$ (crystal structure), gave η^4-vinylallene complexes.

The preparation of transition-metal allylic complexes and trimethylenemethane complexes[1] as well as their synthetic applications[2] have attracted a great deal of attention recently. However, few examples of transition-metal complexes containing co-ordinated conjugated vinylallene[3] have been reported and their synthetic relationship to the above complexes has been mostly unnoticed. In this communication we report the synthesis of a number of vinylallene complexes from the reactions of $[W(cp)(CO)_2\{\eta^4\text{-}H_2CC[C(C{\equiv}CPh)_2]CH_2\}]^+$ **1** (cp = $\eta^5\text{-}C_5H_5$) with various nucleophiles followed by protonation. The nucleophilic addition occurs at the non-substituted terminal carbon of the alkyne ligand and subsequent protonation at the acetylide group. Thus from the reaction of **1** with $[Ru(cp)(PPh_3)_2(C{\equiv}CPh)]$ under mild conditions, the first tungsten–ruthenium dinuclear cationic complex $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(C{\equiv}CPh)_2]CH_2C(Ph){=}C{=}Ru(cp)(PPh_3)_2\}]^+$ **2a** is isolated. Subsequent protonation yields a dinuclear dicationic complex with a $\mu\text{-}\eta^4,\eta^1$-vinylallene–vinylidene bridging ligand.

Complex **1** was prepared from the reaction of $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(OH)(C{\equiv}CPh)_2]CH_2\}]$ with HBF_4 in 89% yield and its reactions with $[Ru(cp)(PPh_3)_2(C{\equiv}CPh)]$, PPh_3 or H^- cleanly produce the allylic complexes $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(C{\equiv}CPh)_2]CH_2R\}]$ [R = $(Ph_3P)_2(cp)Ru{=}C{=}CPh^+$ **2a**, $PPh_3{}^+$ **2b** or H **2c**] at 0 °C in MeCN. All nucleophilic additions occur exclusively at the non-substituted terminus of the trimethylenemethane ligand. In the reaction of **1** with $[Ru(cp)(PPh_3)_2(C{\equiv}CPh)]$ the triple bond of the latter serves as a nucleophilic centre and thus the deep red tungsten–ruthenium dinuclear complex **2a** is produced, see Scheme 1. In the reaction of **1** with PPh_3 the phosphine attacks the same position giving **2b** and **2c** is prepared from hydride addition. The spectroscopic data† for **2** are consistent with their formulations. In the IR spectra of **2a** and **2b** the ν_{CO} absorptions (all less than 2000 cm^{-1}) indicate a neutral $(cp)W(CO)_2$ moiety inferring localization of the cationic charge at the Ru atom and PPh_3, respectively. In the ^1H NMR spectra the *syn* and *anti* protons of **2** appear as two broad resonances in the normal allylic region of δ 3.15–2.70. For **2a** and **2b** the other methylene protons appear as multiplet resonances at lower field (δ 4.61–3.23). In the ^{31}P NMR spectrum of **2a** the resonances of the two PPh_3 ligands appear as doublets at δ 41.8 and 43.1 with J_{PP} = 27.0 Hz, in contrast to a singlet resonance for similar ruthenium complexes[4] which show fluxionality of the vinylidene ligand. The inequivalence of the two PPh_3 in **2a** is attributed to the steric bulk of the tungsten–allyl moiety hindering rotation of the vinylidene ligand.

The structure of complex **2a** was confirmed by a single-crystal X-ray diffraction analysis‡ and an ORTEP[5] drawing is shown in Fig. 1. The Ru–C(24) [1.86(1) Å], C(24)–C(23) [1.31(2) Å] and Ru–C(24)–C(23) [170(1)°] are typical for cationic ruthenium vinylidene complexes. The α,α,β-trisubstituted allylic group adopts an *endo* conformation with W–C (centre) 2.28(1) Å being the shortest among the three W–C

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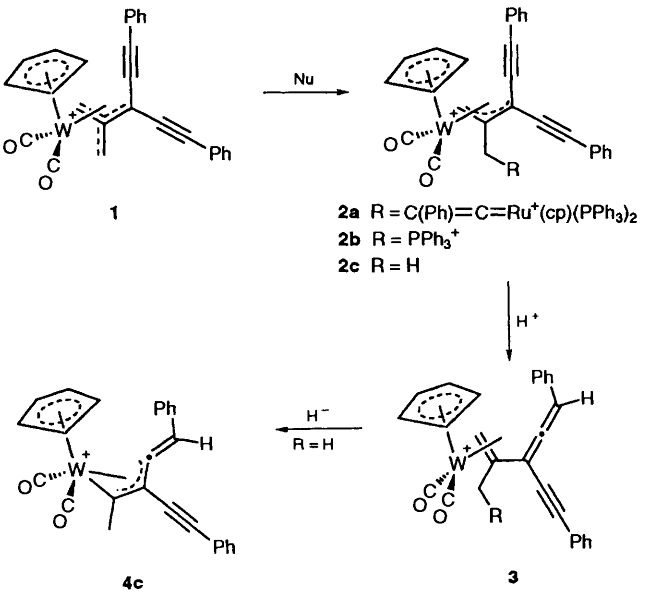
† Proton (300 MHz) and $^{13}C\text{-}\{^1H\}$ (75 MHz) (298 K, CD_3CN, relative to $SiMe_4$, *J* in Hz), ^{31}P (121.5 MHz) NMR (H_3PO_4 external standard). Complex **1**: IR (MeCN) ν_{CO} 2069s, 2022s cm^{-1}; ^1H NMR, δ 7.53–7.38 (m, 10 H, Ph), 5.83 (s, 5 H, cp), 3.77 (s, 2 H, *syn*-CH_2), 3.51 (s, 2 H, *anti*-CH_2); ^{13}C NMR, δ 201.2 (CO), 132.7–129.7 (Ph), 122.1 ($\mathit{C}CH_2$), 93.9 (cp), 90.3 (≡C), 86.5 (≡C), 68.5 ($\mathit{C}C{\equiv}CPh$), 54.5 (CH_2); mass spectrum (FAB), *m/z* 559 ($M^+ - BF_4$), 503 ($M^+ - 2CO - BF_4$). **2a** (Found: C, 55.91; H, 3.54. Calc. for $C_{76}H_{59}BF_4O_2P_2RuW{\cdot}CH_2Cl_2$: C, 56.35; H, 3.35%) IR (MeCN) ν_{CO} 1953s, 1884s cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.37–6.78 (m, 45 H, Ph), 5.34 (s, 5 H, cp), 5.10 (s, 5 H, cp), 3.77 (d, $^2J_{HH}$ = 14.1, 1 H, CH), 3.23 (d, $^2J_{HH}$ = 14.1, 1 H, CH), 2.90 (s, 1 H, *syn*-CH), 2.70 (s, 1 H, *anti*-CH); ^{13}C NMR ($CDCl_3$), δ 134.5–123.5 (Ph), 93.9 (cp), 92.9 (cp), 35.5 ($\mathit{C}H_2CPh{=}$), 29.7 ($\mathit{C}C{\equiv}CPh$), 27.1 (CH_2); ^{31}P NMR ($CDCl_3$), δ 43.1 (d, $^2J_{PP}$ = 27), 41.8 (d, $^2J_{PP}$ = 27); mass spectrum (FAB), *m/z* 1438 (M^+), 1351 ($M^+ - BF_4$), 1033 ($M^+ - BF_4 - PPh_3 - 2$ CO), 771 ($M^+ - BF_4 - 2PPh_3 - 2$ CO). **2b**: IR (tetrahydrofuran, thf) ν_{CO} 1955s, 1884s cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.80–7.23 (m, 25 H, Ph), 5.40 (s, 5 H, cp), 4.61 (dd, 1 H, CH), 4.18 (dd, 1 H, CH), 2.95 (s, 1 H, *syn*-CH), 2.78 (s, 1 H, *anti*-CH); ^{13}C NMR ($CDCl_3$), δ 224.0, 220.9 (CO), 137.1–115.6 (Ph), 94.7 ($\mathit{C}CH_2P$), 93.3 (cp), 90.7 (≡C), 87.7 (≡C), 85.9 (≡C), 82.8 (≡C), 36.2 (CH_2P), 29.5 ($\mathit{C}C{\equiv}CPh$), 27.5 ($\mathit{C}H_2CCH_2P$); ^{31}P NMR ($CDCl_3$), δ 26.7 (s); mass spectrum (FAB), *m/z* 821 ($M^+ - BF_4$), 765 ($M^+ - BF_4 - 2$ CO), 559 ($M^+ - BF_4 - PPh_3$). **2c**: IR (MeCN) ν_{CO} 1952s, 1879s cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.50–7.24 (m, 10 H, Ph), 5.40 (s, 5 H, cp), 3.15 (br, 1 H, *syn*-CH), 2.97 (s, 1 H, *anti*-CH), 2.75 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$), δ 228.8, 224.4 (CO), 131.8–123.6 (Ph), 101.7 ($CH_2\mathit{C}CH_3$), 94.5 (≡C), 92.9 (cp), 92.2 (≡C), 84.4 (≡C), 80.5 (≡C), 29.2 ($\mathit{C}C{\equiv}CPh$), 28.5 ($\mathit{C}H_2CCH_3$), 22.9 (CH_3); mass spectrum (FAB), *m/z* 560 (M^+), 504 ($M^+ - 2$ CO). **3a**: IR (KBr) ν_{CO} 2073s, 2024s cm^{-1}; ^1H NMR, δ 7.68–6.87 (m, 45 H, Ph), 5.68 (s, 5 H, cp), 5.31 (s, 5 H, cp), 4.23 (d, $^2J_{HH}$ = 14, 1 H, $CH_2C{=}$), 3.40 (d, $^2J_{HH}$ = 14, 1 H, $CH_2C{=}$), 2.48 (br, 1 H, $={CH_2}$), 1.81 (br, 1 H, $={CH_2}$); ^{31}P NMR, δ 43.5 (d, $^2J_{PP}$ = 26.6), 41.6 (d, $^2J_{PP}$ = 26.6); mass spectrum (FAB), *m/z* 1439 ($M^+ - BF_4$), 1352 ($M^+ - 2BF_4$), 1324 ($M^+ - 2BF_4 - CO$), 1034 ($M^+ - 2BF_4 - 2\,CO - PPh_3$). **3b**: IR (KBr) ν_{CO} 2068s, 2022s cm^{-1}; ^1H NMR, δ 7.97–7.28 (m, 25 H, Ph), 6.06 (s, 5 H, cp), 5.02 (t, $^2J_{HH} = {}^2J_{HP}$ = 4, 1 H, CH_2P), 4.58 (t, $^2J_{HH} = {}^2J_{HP}$ = 4, 1 H, CH_2P), 2.37 (br, 1 H, $={CH_2}$), 1.65 (br, 1 H, $={CH_2}$); ^{31}P NMR, δ 27.7 (s); mass spectrum (FAB), *m/z* 909 ($M^+ - BF_4$), 822 ($M^+ - 2BF_4$), 766 ($M^+ - 2BF_4 - 2$ CO), 504 ($M^+ - 2BF_4 - 2CO - PPh_3$). **3c**: IR (KBr) ν_{CO} 2067s, 2013s cm^{-1}; ^1H NMR, δ 8.01–7.38 (m, 10 H, Ph), 5.88 (s, 5 H, cp), 2.86 (s, 3 H, CH_3), 2.72 (br, 1 H, $={CH_2}$), 1.86 (br, 1 H, $={CH_2}$); mass spectrum (FAB), *m/z* 561 ($M^+ - BF_4$), 505 ($M^+ - BF_4 - 2CO$). **4c** (Found: C, 57.44; H, 4.01. Calc. for $C_{26}H_{19}O_2W$: C, 57.57; H, 4.12%) IR (MeCN) ν_{CO} 1942s, 1868s cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.95 (s, 1 H, $={CHPh}$), 7.61–7.20 (m, 10 H, Ph), 5.51 (s, 5 H, cp), 2.18 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$), δ 229.8, 215.9 (CO), 154.3 ($\mathit{C}{=}CHPh$), 138.8–122.8 (Ph), 128.7 ($C{=}\mathit{C}HPh$), 94.4 (cp), 91.6 ($\mathit{C}C{\equiv}CPh$), 85.0 ($C{\equiv}\mathit{C}Ph$), 80.9 ($\mathit{C}{\equiv}CPh$), 49.0 ($\mathit{C}CH_3$), 28.1 (CH_3), 27.3 (CH_3); mass spectrum (FAB), *m/z* 562 (M^+), 534 ($M^+ - CO$), 506 ($M^+ - 2CO$).

‡ Crystal data: $C_{76}H_{59}BF_4O_2P_2RuW{\cdot}3CH_2Cl_2$, *M* = 1692.76, triclinic, space group, $P\bar{1}$, *a* = 13.171(4), *b* = 14.797(6), *c* = 19.960(6) Å, α = 92.02(3), β = 100.17(3), γ = 100.39(3)°, *U* = 3757.1(22) $Å^3$, *Z* = 2, D_c = 1.496 g cm^{-3}, crystal dimensions 0.15 × 0.40 × 0.40 mm, μ = 19.107 cm^{-1}, observed reflections 5618 [$I > 2\sigma(I)$], total 9799, $2\theta_{max}$ = 45.0°. An absorption correction was carried out (transmission range 0.858–1.000). The structure was solved by Patterson synthesis then refined by standard least-squares and Fourier-difference techniques; $w = 1/\sigma^2(F_o)$. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Three CH_2Cl_2 molecules per complex molecule were also observed. Total number of parameters: 793. *R* = 0.066, *R'* = 0.069; goodness of fit = 2.64, Δρ = −1.36 to 1.37 e $Å^{-3}$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 Nu = $Ru(cp)(PPh_3)_2(C{\equiv}CPh)$ **2a**, PPh_3 **2b** or $NaBH_4$ **2c**

(allyl) bonds. The newly formed C(22)–C(23) bond of 1.50(2) Å is a normal single bond.

In the protonation reaction of complex **2** the C≡CPh group of the allylic ligand serves as a proton acceptor, thus the η^4-vinylallene product **3** is produced cleanly. For example, protonation of **2a** by HBF_4 gives **3a** in quantitative NMR yield, see Scheme 1. Protonation of **2b** and **2c** also gives **3b** and **3c**, respectively. In the IR spectrum of **3a** the ν_{CO} absorptions, all at $> 2000\ cm^{-1}$, indicate the cationic character of the tungsten centre. In the ^1H NMR spectrum of **3a** the two broad resonances at δ 2.48 and 1.81 are assigned to the two *gem*-vinylic protons. The relatively upfield shift is due to co-ordination of the vinyl group. The two doublets, at δ 4.23 and 3.40 are assigned to the other methylene group. The resonances of the terminal allenyl proton and the aromatic protons are overlapped. The configuration of the phenyl group at the allene terminal is not clear at this time, however judging by the fact that protonation should occur at the most electron-rich site one could reasonably anticipate a *syn* configuration (with respect to W). Namely direct protonation at the acetylide group should be more favourable than protonation at the metal followed by proton transfer. An η^4-vinylallene ligand in an iron complex was reported recently.[6] Two methods are known for the preparation of such complexes: treatment of a vinylketene complex with a stabilized Wittig reagent[7] and simple complexation of vinylallene to a metal.[6] Our method provides another approach for such a compound.

The reaction of an excess $Na[BH_3(CN)]$ with complex **3c** gave neutral **4c** in high yield. Namely, addition of hydride occurs at the terminal CH_2 yielding **4c** with two Me groups, *i.e.* the η^4-vinylallene is converted into an η^3-vinylallylic ligand. In the ^1H NMR spectrum the two singlets at δ 2.18 and 1.67 are assigned to the two methyl groups and the singlet at δ 7.95 with relative integration of 1 H is assigned to the vinylic proton; the assignment was confirmed by a deuteriation study. The ν_{CO} at 1942 and 1868 cm^{-1} indicates the neutral character of the metal centre. Vinyl substituents at allylic terminals are known in a few previous examples.[8] The configuration of the phenyl relative to the allylic group is not known. Similar reactions of **3a** and **3b** give complex mixtures. Owing to the dicationic charges of **3a** and **3b** the addition of hydride might occur at two possible sites. No attempt was made to isolate the product.

We have previously reported the synthesis of the analogous 1,1-dimethyltrimethylenemethane complex[9] $[W(cp)(CO)_2\{\eta^4\text{-}H_2CC(CMe_2)CH_2\}]^+$ **5**, which shows different reactivity from that of **1**. Depending on the nucleophiles used, additions could occur either at the substituted or at the non-substituted site of trimethylenemethane ligand of **5**. For example, the addition of H^- and N_3^- occurs at the substituted site producing $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC(CHMe_2)CH_2\}]$ and $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(N_3)Me_2]CH_2\}]$ respectively. On the other hand, addition of thio nucleophiles occurs at the non-substituted site of **5**, similar to that of **2**. Interestingly, in the reaction of **5** with $[Ru(cp)(PPh_3)_2(C{\equiv}CPh)]$ the acidic proton of the methyl groups in **5** prohibits formation of the addition product, but the deprotonation reaction produces $[W(cp)(CO)_2\{\eta^3\text{-}H_2CC[C(Me){=}CH_2]CH_2\}]$ and the vinylidene complex $[Ru(cp)(PPh_3)_2({=}C{=}CHPh)]^+$.

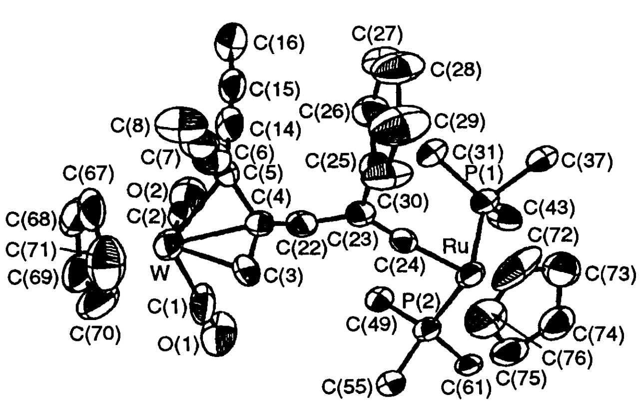


Fig. 1 Structure of the cation of complex **2a** showing the atom numbering scheme and with 50% probability ellipsoids; all the phenyl groups of the phosphine and of the allylic ligand are omitted for clarity. Atoms C(8), C(16), C(31), C(37), 3(43), C(49), C(55) and C(61) are the *ipso* phenyl carbons. Only the phenyl group of the vinylidene ligand is shown

In summary, in the reaction of the cationic 1,1-di(phenylethynyl)trimethylenemethane complex with nucleophiles, the electron-rich acetylide group controls the site of nucleophilic addition. Furthermore, subsequent protonation at this group also provides an entry to a rare class of vinylallene complex. The synthesis and reactivity of these complexes are currently under investigation.

Acknowledgements

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